Investigation on the coloring and bleaching processes of WO_{3-x} photochromic thin films

Marie Bourdin,^{a,b} Guillaume Salek,^b Alexandre Fargues,^a Sandra Messaddeq,^b Younes Messaddeq,^b Thierry Cardinal,^a Manuel Gaudon,^{*a}

WO_{3-x} (oxygen deficient tungsten oxide) thin films and WO_{3-x} / Ta₂O₅ (tantalum oxide) composite films exhibit a huge photochromic effect with 60% of near-infrared transmission modulation, in comparison to literature reviews. The colouring efficiency of such film results from both the stoichiometry of the particles (oxygen/tungsten deficient ratio) and the quality of the films (films are thin, homogeneous, constituted of nanoparticles about 5 nm diameter and so with low scattering). Additionally, the high colouring efficiency obtained with a low fluence ultraviolet (UV) lamp, is followed by a nearly complete bleaching phenomenon after few hours in dark. Beyond the attractiveness of our films toward multiple applications, and especially as films able to regulate the solar flow through smart windows, the optical properties and the colouring and bleaching kinetics were deeply investigated. Whatever the WO_{3-x} thin films or the WO_{3-x} / Ta₂O₅ composite films, colouring under irradiation as well as bleaching under dark, are phenomena which both proceed with a complex kinetic combining ultra-fast process (from charge transfers, with characteristic time about the minute) and slower process (linked to ionic diffusion, with characteristic time about the hour or even longer).

1. Introduction

Photochromism is the ability for a material to change its coloration in a reversible way under light irradiation. The photochromic materials can be divided into two main groups: organic materials, such as spiropyrans, azobenzenes or diarylethenes¹⁻⁴, and inorganic materials such as transition metal oxides, metal halides or rare earth complexes⁵⁻⁸. Several chemical processes, induced by irradiation, can lead to the color change of the compound. For inorganic materials, photochromic phenomena are essentially linked to a photo-induced redox process.

Inorganic photochromic materials are generally transition metal oxides. These oxides are large gap semiconductors (between 2.5 and 3.5 eV) like the molybdenum, niobium, vanadium or tungsten compounds: MoO₃^{6,9-12}, Nb₂O₅^{13,14}, V₂O₅^{15,16} or WO₃^{5,17-21}. Regarding more particularly the tungsten oxide, Deb was the first to highlight the photochromic properties of the WO₃ thin films, in 1973⁵. Although WO₃ is not the preferred material for working on photochromism, compared to MoO₃, which exhibits better photochromic effect in terms of contrast and kinetic. Indeed, despite of the weak optical contrast between colored and bleached states as well as its very slow and incomplete bleaching process (lack of adequate reversibility for many applications), WO₃ oxide is more and more studied. Indeed, from the optimization of crystallite morphologies, recent studies have been carried out showing a particular interest for producing photosensitive and reprintable inks^{22,23} based on WO₃ as nanoparticles.

The mechanisms governing photochromism in transition metal oxides are complex and are not fully understood yet, at least they remain a subject to controversies. However, the literature reports

agreed on the fact that the photochromism mechanism is induced for irradiation wavelengths allowing the transfer through the semiconductor forbidden band with the creation of an exciton, i.e. for light energy in UV range for WO₃ oxide since the gap between valence and conduction band is located at the border between UV and visible range for this oxide. In 1973⁵, Deb has proposed a complete model explaining the photochromic effect in WO₃ films under UV irradiation. Deb proposed that the photochromism is linked to the creation of colored centers during the preparation of the film. These colored centers would trap the photo-induced free electrons leading to the coloration of the material. Several studies were carried out²⁰⁻²⁴, it is now well established that the blue color in WO₃ issued from the photo-reduction of the material is based on the transfer of electrons between tungsten ions having different valence states (W⁶⁺, W⁵⁺) via an intervalence charge transfer (IVCT). The photo-redox process follows the next steps. When the WO₃ film is irradiated with UV light, electrons (e⁻) and holes (h⁺) are generated (excitons). Then, sufficiently slow charge depletion occurs, allowing separate reactions of the initiated electrons and holes, additionally to photo-excitons recombination which remains the main. Thus, few electrons are then trapped by some tungsten ions, leading to W⁵⁺ ion formation, so IVCT phenomenon and blue coloration. IVCT is associated with the creation of an absorption site with energy corresponding to the frontier between visible range and near infrared, and with the blue coloration of the material^{20,24}. In literature, it is often suggested that the holes would then react with the water adsorbed on the WO₃ film surface to form the H⁺ ions (water oxidation); these protons would then diffuse into the material, thus creating a tungsten bronze with H_xWO₃ chemical formula. This model explains the stabilization of the reduction of a

fraction of the W^{6+} ions into W^{5+} ions thanks to their association with the integration of protons inside the WO_3 crystalline network. Nonetheless, the latter model is in default to explain the bleaching process while maintaining the material in dark, which runs like the reverse redox equation and so implies the deprotonation. Although most of the studies devoted to the photochromism of WO_3 agree and re-propose the Deb's process, all the parameters necessary to see the appearance of photochromism are not certain. For illustration, recent studies have shown that photochromism only appears if the WO_3 oxide previously exhibits oxygen vacancies^{25,26}. Gérard et al. have shown that perfectly stoichiometric WO_3 films have a very weak photochromic effect compared to films that are slightly deficient in oxygen²⁷. Other authors have shown that water must be initially chemisorbed on the film's surface²⁸ or even directly incorporated as crystalline water groups into the material such as in the $WO_3 \cdot 0.33H_2O$ ²⁹ to observe efficient photochromism. With the aim to determine which parameters could lead to an improvement in the photochromic performances of WO_3 , a new generation of studies have focused the effort on the evaluation of many factors which can influence photochromic behavior, such as heat treatment, the presence of doping ions³⁰ or adsorbed water^{28,31}. The different film preparation techniques can also lead to slight modification on the forbidden band energy, the chemical compositions and the film microstructures, thus leading to different photochromic performances. It has also been shown that particle size plays a predominant role on the photochromism intensity. Indeed, particles of small sizes and therefore having a large specific surface are shown to be more photo-reactive³². The impact of the WO_3 particle shape has also been studied: nanosheets or nanoflocons, with large specific surfaces, have a good photoreactivity with faster coloration process^{22,33}. The comparison of photochromic contrast obtained from the different available crystal structures for WO_3 oxide: cubic, hexagonal, monoclinic systems^{31,34}, have shown that the optical contrast is linked to the structural feature.

In this article, we propose to study the photochromic properties of thin films of WO_3 obtained by dip-coating from suspended nanoparticles in ethanol. In the first part, the discussion focuses on the film elaboration. In a second part, the photochromic behavior of two types of film is compared and deeply analyzed: on the one hand a WO_3 pristine film, and on the other hand a sandwich film constituted by a WO_3 sub-layer covered with a Ta_2O_5 top-layer. Finally, the last section is devoted to the reversibility aspect of the photochromism of the two previous films.

2. Experimental

2.1. Synthetic procedures

WO_{3-x} film elaboration. Chemical reagents were purchased from Sigma Aldrich and used as received. Tungsten (VI) chloride was used as tungsten source and diethylene glycol (DEG) as solvent. WCl_6 (7,2g) was added to 100mL of DEG and 20mL of distilled water. The mixture was heated at 180°C with continuous stirring and refluxed for 3h. At the end of the reaction, a deep blue precipitate was obtained. The precipitate was washed and centrifuged several times with ethanol to remove any trace of solvent and dried in an oven at 80°C and

then was washed in HCL solution (1 mol.L⁻¹) for surface functionalization with protons. The functionalized WO_{3-x} nanoparticles (NPs) were then dispersed in ethanol to prepare the suspensions (weight content in NPs is 86 g.L⁻¹) which are dip-coated on standard glass substrate to obtain pristine WO_{3-x} thin films. The dip-coating parameters are (i) the dip-coating speed: 133mm.min⁻¹ and (ii) for multilayers, successive dip coating steps are operated with between two steps 30 min drying in an oven (90°C).

Ta_2O_5 and film elaboration. Chemical reagents were purchased from Sigma Aldrich and used as received. Tantalum ethoxide was used as Ta source and anhydrous ethanol as solvent. The sol is obtained from tantalum ethoxide, anhydrous ethanol, 37% hydrochloric acid and distilled water. The protocol consists in preparing two separate solutions before mixing to obtain a stable sol. In solution A, 1 g of tantalum ethoxide is added to 4.92 ml of anhydrous ethanol, and stirred for 10 min. In solution B, 2.46 mL of ethanol is mixed with 0.0664 mL of distilled water and 0.01 mL of hydrochloric acid. After mixing, by adding solution B, drop by drop, into solution A, the as-prepared sol is stirred for 1 hr. Once the sol was prepared, films were made by dip-coating with a deposition rate fixed at 133 mm.min⁻¹. The layers are dried after each deposition for 30 min. at 90 ° C. Deposition of one to four successive layers have been made.

Ta_2O_5 / WO_{3-x} composite film elaboration. "sandwich design" with WO_{3-x} film covered by a Ta_2O_5 as top-layer are discussed.

2.2. Characterization techniques

Chemical, structural and morphological characterizations. WO_{3-x} chemical composition of the as-prepared powder can be determined thanks to chemical titration. The chemical titration was made after dissolution of the powder in NaOH aqueous solution within presence of $KMnO_4$ and KI salt dissolved in large excess in regard of the tungsten trioxide concentration. Redox process between MnO_4^- and W^{5+} ions and then between the rest of MnO_4^- and I^- lead to the formation of I_2 species which can be titrated by $Na_2S_2O_3$ solution in order to get W^{5+} concentration, and then to deduce the oxygen sub-stoichiometry in WO_{3-x} compounds (x equals half time the W^{5+} concentration).

Zeta potential, which corresponds to the potential of the particles located at the sliding plane between the layer of Stern and the diffuse layer, is measured basing on the electrophoretic mobility of the particles in aqueous solution with different pH values with a Zetasizer NanoZS (Malvern). With the same apparatus, Dynamic light scattering (DLS) was used to determine the size distribution profile of the WO_{3-x} particles in the suspensions used for dip-coating process.

The NPs and the film structures were characterized by X-ray diffraction analysis (PANanalytical X'Pert Pro instrument Cu $K\alpha_1 = 1.54056 \text{ \AA}$, $K\alpha_2 = 1.54439 \text{ \AA}$ and 2θ range from 8° to 80°). The morphology of the as-prepared films was studied using Scanning electron microscopy (SEM) (Quanta 3D FEG) working

at 5 kV acceleration voltage. Film thickness was measured using an optical profilometer WYCO NT1100 (Veeco).

Irradiation condition. Irradiations were performed using a UV Hg-lamp (Vilbert Lourmat 8.LC) at a monochromatic wavelength of 365 nm. The sample is placed at 10 cm from 8 W tubes: the power per surface unit received by the sample is equal to 5.6 W/m², i.e. irradiance close to the UV-daylight irradiance in London. The use of such low fluence is to be near the real condition, in regard of life-conditions the smart windows or smart textiles are exposed.

Optical characterization. Film transmission spectra were recorded at room temperature from 200 to 2500 nm on a Cary 5000 spectrophotometer using an integration sphere (spectral resolution: 1 nm and band width: 2 nm).

3. Results and Discussion

3.1. Film elaboration

WO_{3-x} suspensions. The WO_{3-x} nanoparticles, with a pale blue color, were already described in terms of morphology, structure and chemical composition in our previous paper devoted to the comparison of the photochromic efficiency of various WO₃-type powders³⁵. The amount of W⁵⁺ within the raw material, was determined using an iodometric titration. The tests have given an average x value of 0.018, leading to the formula of the raw powder W⁶⁺_{0.982}W⁵⁺_{0.036}O_{2.982}. The structure was shown to be pseudo-cubic with *a* unit-cell parameter about 3.80 Å. The particle sizes exhibit a narrow distribution centred around 4-5 nm diameter.

Preliminary works to obtain some stable WO_{3-x} NPs suspensions are firstly conducted (Fig.1).

The suspension obtained with the particles extracted from the precipitation medium (DEG) with simple washing with ethanol were sedimenting very quickly. It was necessary to develop a strategy for the preparation a more stable suspension. First, the determination of the isoelectric point of the WO_{3-x} particles, was performed. Zeta potential values of the particles obtained as a function of the pH of the aqueous solution are shown in Fig. 1a. The isoelectric point of our particles is at a very acidic pH of 1.5 as already listed in the literature^{36,37}. Note that this can be interpreted as characteristic of a particle surface very rich in cations (W⁶⁺, W⁵⁺), the surface therefore has a very clear tendency for hydroxylation at the expense of protonation. Cation-rich surfaces are in good agreement with the WO_{3-x} oxygen-deficient stoichiometry: a segregation of the oxygen vacancies at the surface may also be considered. Furthermore, zeta measurements show that the particles sediment easily for suspensions of pH between 1 and 2.2 (generally a suspension is said to be stable when the potential, in absolute value, is greater than 20 mV); suspension is stable for pH between 2.2 and 6. In this range, the particles exhibit negatively-charged surfaces due to the formation of pending bonds between the surface tungsten ions and OH⁻ hydroxyl groups. For pH values higher than 5-6 the particles are gradually dissolved since the paradoxical rise in surface potential between pH between 4 and 6 (the surface charge

becomes less negative) can be seen as a sign precursor to dissolution, with transformation of the nature of the dispersed particles: transition from tungsten oxides to tungsten hydroxides. This measurement in aqueous solution allowed us to develop a protocol for stabilization of our particle suspensions in ethanol. Once the ethanol washes carried out, the particles were washed two additional times in distilled water, the goal being to negatively charge the surface of our particles (hydroxyl group fixation). The particles were subsequently re-suspended in ethanol. The final suspension obtained is blue and much more stable against sedimentation, even over long periods of time (more than 4 weeks). In order to illustrate the influence of such an hydroxyl functionalization of the WO_{3-x} NPs surfaces on the particles, a quasi-elastic light scattering (DLS) measurement was performed on two suspensions, respectively with particles which are water-washed and not water-washed (results reported in Fig. 1b).

Figure 1: a) Evolution of the zeta potential of the WO_{3-x} particles according to the pH. b) Size distribution of WO_{3-x} particles in suspension with (ii) or without (i) hydroxyl group fixation.

WO_{3-x} film elaboration. The WO_{3-x} films are prepared from 86 g.L⁻¹ suspension with hydroxylated particles. The photographs and transmission spectra show that the films from the modified suspension present a good visible transmission with a low scattering coefficient (Fig. 2a). In the near infrared, the

transmission at 1200 nm varies from 80% for 1-layer film to 62% for 6-layer film (1-, 2-, 3-, 4-, 5- and 6- layer films were studied). From the 3-layer film, a distinct absorption band appears centred at 1200 nm; this absorption band is linked to the presence of W^{5+} ions due to the intervalence charge transfer (IVCT) between W^{5+} and W^{6+} ions in the structural network of the WO_{3-x} particles. As the photochromism is related to the increase of these IVCT charge transfer band, the thickness reached from the 3-layer coating is enough to carry out photochromism studies. The thickness measurements performed with optical profilometer allow assessing the thickness evolution of the films versus the number of successive coatings. The thickness variation is nearly linear with the number of deposited layers (Fig. 2b). The SEM images of our coatings (top views), reported in Fig. 3, show that the surface of the films has an adequate density; however, the presence of cracks, in particular on films for the 6 layers film, is evidenced.

Figure 2: SEM pictures of the films.

Figure 1: a) Transmission spectra and photographs of WO_{3-x} films, b) evolution of the thickness of the films according to the number of layers.

Ta₂O₅ film elaboration. The films obtained from 1 to 4 successive coating in Ta₂O₅ sols were characterized with the same procedure as the WO_{3-x} films i.e. by transmission spectra, photographs, thickness measurements and SEM (top views) images. X-ray diffraction shows no diffraction peaks, the Ta₂O₅ films are amorphous.

The transmission spectra (Fig. 4a) show that the four films studied are transparent with a transmission in the visible range of more than 80%; even with the increase the number of successive deposits. In addition, the appearance of interference fringes, (with a single very wide fringe for films from one or two successive deposits and two clearly visible fringes for films from three or four deposits) is also a sign that the surface of the films is very smooth and the film thicknesses are very regular. Indeed, the interference fringes only appear when the film roughness is low, and the thickness is enough regular to allow consistent interference between the multiple reflections appearing at the different film / air interfaces. The thickness evolution versus the number of successive deposits is roughly linear (Fig. 4b), and SEM images resolution is not sufficiently to evidence any defects (cracks or roughness): films are smooth and crack-free.

From these data and using the method proposed by Swanepoel³⁸ (illustration figure 4c) it is possible to estimate the value of the refractive index of the film of Ta₂O₅ from the envelope which includes the interference fringes, i.e. from the minimal and T_M maximal transmission values in the interference regime and the substrate index from equations:

$$n = (N + (N^2 - n_s^2)^{1/2})^{1/2} \quad (n_s = 1.52)$$

$$\text{with } N = 2 \times n_s \times (T_M - t_m) / (T_M \times t_m) + (n_s^2 + 1) / 2.$$

Thus, the effective refractive index of the Ta₂O₅ film can be estimated to 1.9 (at a wavelength of 600 nm). In regard of the theoretical refractive index of tantalum oxide: 2.23³⁹, the estimated effective refractive index indicates that quite dense films are obtained, with about 15-20% of porosity (considering that the effective index can be calculated as a mixing law of porosity and Ta₂O₅ particle linear susceptibilities).

Figure 4: a) Transmission spectra and photographs of Ta_2O_5 films, b) evolution of the thickness of the films according to the number of layers, c) Illustration of the Swanepoel plot for the evaluation of the refractive index.

WO_3-x / Ta_2O_5 composite film elaboration. The method chosen to make composite films is to prepare “sandwich-type” films, i.e. on a 1 to 6-layer WO_3-x film, a single top-layer of Ta_2O_5 is then coated. The idea is to fill surface defects of the WO_3-x films with the Ta_2O_5 additional layer, in order to limit the film scattering phenomenon thanks to the proximity of the refractive indices of these two compounds. In addition, the top layer of tantalum oxide also constitutes a protective layer of

the film of tungsten oxide particles (particularly regarding oxidative attack: hydration, from the outside medium). From the transmission spectra (Fig. 5a), several elements deserve discussion. The good transparency in the visible area of films, already demonstrated by the photographs of these films, is confirmed by the transmission spectra. The appearance of interference fringes, implying multireflection effect within the film, indicates that the optical quality (roughness) of the film surface is greatly improved by adding the Ta_2O_5 layer. Moreover, the absorption band relative to the presence of W^{5+} ions (IVCT), centred at 1200 nm, is now visible for films made of successive deposition steps greater than 3 layers. Analysis of the surface of the films by scanning electron microscopy (Fig. 5b), also shows that the surface roughness of the films is improved by the additional layer of Ta_2O_5 oxide.

Figure 5: a) Transmission spectra and photographs of WO_3-x / Ta_2O_5 composite films, and b) SEM pictures of the films.

Nonetheless, a significant roughness and small cracks linked to the tungsten oxide bottom layer (especially visible on high magnification images) remain visible. For less than 2 successive coatings of tungsten oxide, the cracks are no longer visible. On the other side, there is also deadhesion of the films from the substrate for films issued from 5 and 6 successive coatings of tungsten oxide. This delamination phenomenon can be linked to a higher chemical affinity of the WO_3-x layer with Ta_2O_5 than with the silica glass substrate. Constraints created during gelation of the Ta_2O_5 top-layer (during the sol-gel transition), can spread to the interface between the WO_3-x film and the substrate. Recent studies performed in our laboratory

have shown that this delamination can be cancelled by depositing as a first primer, a layer of Ta₂O₅. Such Ta₂O₅ / WO_{3-x} / Ta₂O₅ architecture is in prospect. In the following, the 4-layer WO_{3-x} recovered with Ta₂O₅ top-layer, representing a good compromise between a strong IVCT absorption and low scattering will be studied.

3.2. Photochromic properties

Photo-induced colouring of WO_{3-x} film. The photochromic study has firstly focused on the 4-layer WO_{3-x} pristine film for which the IVCT in the near infrared region is already visible before irradiation. The film was submitted to different irradiation durations (cumulated) (Fig. 6a).

We notice firstly that the irradiation makes the film "reacting" in the visible and near-infrared ranges with higher reactivity in the near-infrared region. Nevertheless, the absorption of a part of the red light under irradiation produces a pale blue coloration of the films. This well suggests a significant increase of W⁵⁺ ions. The photo-redox process is herein the origin of a "huge photochromic phenomenon" for such a thin film in regard of the literature devoted to WO₃ photochromism. Indeed, an important increase of the absorption at 1200 nm (1 eV) with a loss of more than 8% of transmission after only 10 seconds of irradiation is observed (when this decrease is only 0.25% at 600 nm (2 eV), showing a poor photochromism in the visible range). Similarly, after 2.5 hours of irradiation, the transmission decreased by 62% at 1200 nm.

Considering that the initial absorbance of the film as the reference, the transmission curves were converted in relative gained absorption of the WO_{3-x} film (Fig. 6b). This conversion of the transmission of the film-substrate sandwich into the selective absorption of the film allows a de-summation in Gaussian peak of the large absorption IVCT band (Fig. 6c).

To try to assign each phenomenon to a specific region of the spectrum we have de-summed the spectra with Gaussians to determine the number of phenomena involved in the photochromism of WO_{3-x} oxide films. For this de-summation, data are plotted vs energy, then treated between 0.62 eV and 2 eV (2000 nm - 620 nm) to include the whole part of the spectrum reacting to UV radiation. The absorption bands are simulated by Gaussian according to the following relation:

$$y = A \times \exp \left\{ -\frac{1}{2} \times \left[\frac{(x - x_c)}{w} \right]^2 \right\},$$

with y is the absorbance, A is the magnitude of a Gaussian contribution in absorbance unit, x the energy in eV, x_c the position of the Gaussian curve in energy, w the width of Gaussian curve in energy. To obtain satisfying simulation, *i.e.* a fit of the experimental absorbance envelope with low reliability factor, three Gaussian curves, partially convoluted, must be used. The 3 Gaussians have the following positions (see Table 1): the main one (Gaussian curve #1) is centred on 1.14 eV (1090 nm); this main peak is surrounded by two satellite signals, located respectively at lower energy, around 0.78 eV (1600 nm), and at higher energy, around 1.53 eV (810 nm). The hypothesis put forward to justify the consideration of 3 Gaussians is difficult to definitively establish. As far as we know, none report of such deep investigation can be found in the literature. The partial convolution of three absorption

bands means three different absorption phenomena. The absorption can come from polaronic transfers (IVCT band), but also from the formation of an electronic gas (plasmonic band linked to Drude's theory). Here, the appearance of the high energy component (band located on 1.5 eV), potentially could be attributed to plasmonic effect related to the appearance of free electrons. The existence of the other two sub-bands can be attributed to two different polaronic transfers. One may propose that these two bands correspond respectively to bulk and surface polaronic transfers (nonetheless, it can be also related to a polaronic transfer involving W⁵⁺ ion neighbouring oxygen vacancies get a specific energy).

Figure 6: Evolution of a) the transmission of the WO_{3-x} film coated on glass substrate and b) the absorbance of the WO_{3-x} film during irradiation. c) De-summation of the WO_{3-x} film absorbance spectrum by three Gaussian curves (for 2h30 of irradiation).

Table 1: Results of the fit of the absorbance of the WO_{3-x} film with three Gaussian curves.

2h30 irr.	Gauss 1	Gauss 2	Gauss 3
Abs. (A) (a.u.)	0.49	0.19	0.27
Width (w) (eV)	0.21	0.3	0.2
Position (x _c) (eV)	1.14	1.53	0.78

The magnitude *A* of these bands roughly evolves versus irradiation time with quite the same kinetics. Nonetheless, some slight differences, especially the Gaussian curve #3 evolves with a lower kinetic than the two other ones, explain the slight blue shift of the maximum of the absorption envelop versus the irradiation time. Thereafter the plot of the evolution of the absorbance at 1 eV (1200 nm), i.e. corresponding to the central position of the complex absorption phenomenon appearing under irradiation is used to investigate more accurately the photo-redox kinetic. It can be noted that for all the kinetic studies that will follow, the choice to work on absorbance spectra rather than transmission spectra is justified by the fact that the absorbance phenomenon is directly related to the concentrations of chromophore species.

Overall, absorbance seems to be changing rapidly in the first minutes of irradiation, then seems to slow down after a few tens of minutes until almost no longer evolve after 2 hours. From a macroscopic point of view, the evolution in term of amplitude of the photo-induced absorbance signal shows an asymptotic evolution. To go further, the absorbance evolution at 1 eV versus the irradiation time is depicted on Figure 7. The experimental plot has been fitted by trend curves (considering a combination of two 1st order kinetic laws), according to the equation: $y = A_1 \times [1 - \exp(-t/k_1)] + A_2 \times [1 - \exp(-t/k_2)]$, With two characteristic times (k_1 and k_2) associated to the phenomena with each their own amplitude (A_1 and A_2). Table 2 summarizes the four working parameters (A_1 , k_1 , A_2 , k_2). The evolution is composed of a fast-kinetic answer (k_2 is about the minute), and a slow-kinetic answer (k_1 , of predominant impact for long irradiation times, is about the hour). The fast and the slow phenomena get roughly the same amplitude (A_1 and A_2 are around 0.3 in absorbance unit). For the energy considered (1 eV) the k_2 parameter monitors mainly the answer of the material during the first minutes of irradiation and is significantly smaller than the parameter k_1 . The independent plot of each fast-kinetic and slow-kinetic exponential contribution allows the schematization of this complex kinetics: the pink curve is associated with (A_2 , k_2) exponential, it increases very quickly in the first seconds and then stabilizes after a while 5-10 minutes of irradiation. Blue plot for (A_1 , k_1) exponential continues to increase even for long-time irradiation; this 2nd phenomenon has not reached saturation (asymptotic value) even after 150 hours. These two different evolutions (fast- and slow-kinetics) can be associated to two different photochromic phenomena : during the first minutes a very pronounced reaction from the surface of the film (the charge transfer being the rate-limiting step)

and with for longer times, a reaction rate-limited by the cationic renewal of the WO₃ particle surfaces (kinetics of a diffusional nature). Indeed, the quick photo-reduction of surface cationic species (photo-reduction from W⁶⁺ to W⁵⁺ ions) would saturate with the increase of the W⁵⁺ surface concentration ; to go further, the surface must "desaturate" by ionic diffusion of the W⁵⁺ surface ions towards the bulk, which leads to slower reaction speed. The photoredox reaction so proceeds with two reaction speeds is depicted in Figure 8.

Figure 7: Absorbance evolution at 1eV (1200nm) during irradiation

Table 2: Kinetic parameters extracted from the fit of the absorbance evolution during irradiation at 1eV

A_1 (a.u.)	k_1 (min)	A_2 (a.u.)	k_2 (min)
0.29	35.13	0.32	1.65

Figure 8: Simplified scheme of the photoreduction of tungsten ions associated with photochromism.

It can be seen that taking into account a very simplified model with two cations on surface and two cations in material bulk, different phenomena can occur during the irradiation to produce a photo-redox reaction with the reduction of the two W^{6+} ions and charge migration to the bulk. Finally, the observation of equivalent amplitudes for the two phenomena (fast and slow), palpitates for the bulk and surface attribution. Indeed, particles of 5 nm of diameter like those constituting the as-prepared films get roughly 50% of ions located on surface.

Photo-induced colouring of WO_{3-x} / Ta_2O_5 composite film. The photochromic study has then focused on the 4-layer WO_{3-x} recovered by a Ta_2O_5 top-coat to evaluate the impact of the tantalum oxide top-layer on the photochromic effect. Indeed, this quite dense and glassy film could act like a barrier and avoid the participation of the atmospheric water molecules to the photo-redox reaction associated to the photochromism.

Using same irradiation conditions and source, the same investigations than for the WO_{3-x} pristine films were carried out on the composite films, transmission versus irradiation, absorbance versus irradiation time and de-summation of the absorbance bands are reported in Figure 9.

We notice that the composite film reacts in the near infrared but less markedly than for the WO_{3-x} pristine film. In fact, after 2 hours of irradiation, the maximal decrease in transmission at 1200 nm is only 28% as compared to the 62% drop observed in the case of the WO_{3-x} film alone. Similarly, the film reacts truly little in the range of visible, the film is not coloured by the radiation. It seems that the phenomenon at high energy (which was attributed to the creation of an electronic gas: plasmonic: Gaussian curve #3) is not observed by adding the Ta_2O_5 top layer. Such phenomenon is probably causally linked to the lower amplitude of the photochromic effect: the concentration of free carriers (or W^{5+} ions) remains probably insufficient to produce the creation of free electron gas. As previously made for the WO_{3-x} pristine film, the spectra were de-summated up in the range 2000 nm - 620 nm (0.62 eV - 2 eV). The de-summation of the transmission spectra allows the determination of the number of convoluted Gaussians and therefore the number of photo-induced chromophores occurring in the composite film for the sandwich configuration. Two Gaussian curves are only necessary; the Gaussian curve parameters are reported in the table 3.

Adding a layer of Ta_2O_5 on the surface of the WO_{3-x} film well limits the amount of photo-reduced tungsten VI ions. The Ta_2O_5 film being transparent to the irradiation lengths, it has, a priori, none effect on the creation of the concentration of exciton pairs in the tungsten oxide semi-conductor. Therefore, the addition of a Ta_2O_5 surface film could limit the charge depletion (between valence band h^+ holes and conductive band free e^-) and acts in favour of the exciton rapid recombination (thus, the photochromic effect is decreased). The photo-reduction of W^{6+} to W^{5+} ions on one side, and/or the oxidation which is necessary to loop the redox process on the other side, are partially impeded. We believe that the top-layer contribution acts on this latter oxidation step: either in avoiding holes recombination with air water molecules (basing

on Deb's mechanism), or in avoiding the surface O^{2-} anions departure in the form of dioxygen (what we assume to be the half-oxidation to compensate for tungsten photo-reduction, tests have shown that the humidity of the surrounding atmosphere is of a negligible impact).

Figure 9: Evolution of a) the transmission of the WO_{3-x} / Ta_2O_5 film coated on glass substrate and b) the absorbance of the film during irradiation. c) De-summation of the film absorbance spectrum by three Gaussian curves (for 2h30 of irradiation).

Table 3: Results of the fit of the absorbance of the WO_{3-x} / Ta_2O_5 film with two Gaussian curves.

2h30 irr.	Gauss 1	Gauss 2
Abs. (A) (a.u.)	0.10	0.05
Width (w) (eV)	0.21	0.25
Position (x_c) (eV)	0.95	1.32

Moreover, the kinetics of the photochromic phenomenon was also investigated; the absorbance evolution at 1 eV versus the irradiation duration is depicted on Figure 10.

Figure 10: Absorbance evolution of $\text{WO}_{3-x} / \text{Ta}_2\text{O}_5$ film during irradiation at 1 eV (1200 nm)

As compared to the previous results obtained on WO_{3-x} pristine films, the main new phenomenon to note for the $\text{WO}_{3-x} / \text{Ta}_2\text{O}_5$ composite films is the increase of the absorption up to 25 minutes of irradiation followed by its gradual decrease after 45 minutes. This overly complex kinetic cannot be fitted considering standard exponential law. The bleaching effect occurring for long irradiation time, acting as a “negative photochromic effect”, was never reported, as far as we know, in literature devoted to inorganic oxide’s photochromism. This negative photochromism can be explained by the re-oxidation of the tungsten ions (W^{5+} to W^{6+} oxidation) from an anionic diffusion coming from the Ta_2O_5 film. Indeed, Ta_2O_5 would behave as a potential source of O^{2-} anions which facilitates the reoxidation of WO_{3-x} films.

Bleaching and cycling. After studying the colouring behaviour of the film as a function of duration of irradiation, we investigated its reversibility. Data from the literature report that the reversibility kinetics are very slow when the product is only left in a dark environment to relax and it is often necessary to heat the film at 80°C - 100°C in air or under ozone to obtain a complete relaxation^{20,22,40}. Herein, the pristine or composite films were previously irradiated for 2 hours (slightly beyond saturation time) at room temperature and let in dark for self-bleaching, directly in the spectrometer chamber in order to record the evolution of the transmission spectra: an analysis is automatically performed every hour. The calculated absorbance spectra are shown in Figure 11 and Figure 12, respectively for the WO_{3-x} pristine film and the $\text{WO}_{3-x} / \text{Ta}_2\text{O}_5$ composite film.

The time necessary for a total return seems very long (out of the investigated time domain), the gap between the spectrum

obtained after 16 hours darkening and the spectrum of the initial state is still important: the maximal absorption after 16 hours darkening being respectively around 1200 nm equal to about 0.3 and 0.2 for WO_{3-x} pristine film and the $\text{WO}_{3-x} / \text{Ta}_2\text{O}_5$ composite film, respectively. The absorbance evolution at 1 eV (1200 nm) versus darkening time are plotted in Figure 11b and The variation of the absorbance has been simulated using the following equation: $y = A_1' \times \exp(-t/k_1') + A_2' \times \exp(-t/k_2')$, i.e. considering as for the colouring effect under irradiation, a double kinetic (slow- vs fast-process) for the bleaching process. Fitting parameters are reported in Table 4.

Table 4: Kinetic parameters extracted from the fit of the self-bleaching evolution at 1 eV after 2h irradiation.

WO_{3-x} pristine film			
A_1' (a.u.)	k_1' (min)	A_2' (a.u.)	k_2' (min)
0.56	21.78	0.23	3.78
$\text{WO}_{3-x} / \text{Ta}_2\text{O}_5$ composite film			
A_1' (a.u.)	k_1' (min)	A_2' (a.u.)	k_2' (min)
0.37	20.57	0.11	4.82

The trends of the two plots and so for the extracted kinetic parameters for WO_{3-x} pristine film and the $\text{WO}_{3-x} / \text{Ta}_2\text{O}_5$ composite film are nearly similar. Indeed, for both films, the parameters k_2' and k_1' corresponding to the relaxation rates of the fast- and slow-bleaching processes are about 3-5 hours for the fast relaxation and of the order of the day (20-22 hours) for the slow phenomenon. Also, the ratio between fast and slow phenomenon amplitude: the A_2'/A_1' ratio, is about 1/3 in both cases. Time necessary for the film to return to its initial state is however very long, but the quality of the fit with a bleaching equation as a convolution of two decreasing exponential terms, show that 100% bleaching is predicted (i.e. no positive value as final asymptotic point has to be taken into consideration in our kinetic equation). The phenomenon of re-oxidation of W^{5+} to W^{6+} by the oxygen in the air is therefore very slow (k times about few hours) compared to photo-reduction of W^{6+} to W^{5+} under UV irradiation (k times of few minutes). Furthermore, the occurrence of slow and fast-colouring processes has been previously interpreted by a fast charge transfer circumscribed to the film surface followed by surface renewal from ionic diffusion (slow process). Logically, the re-oxidation should follow the same pathways with a rapid process involving the W^{5+} ions located on the film surface followed by a slow process dealing with W^{5+} species initially located in bulk progressively diffusing to the surface before to be re-oxidized.

Finally, cycling test were carried out on the WO_{3-x} pristine film design (Figure 13). Several irradiation steps were applied (2 hours irradiation, allowing the colouring process saturation), with sufficient time in dark in between two successive irradiation steps to let the compound fully self-bleached (allowing the film to return to its “initial” state between each irradiation step). The relaxation time between the first and the second cycle is so fixed to 72 h, and 120 h was necessary between the second and the third irradiation.

Figure 3: a) Bleaching of the WO_{3-x} pristine film versus time in dark and b) corresponding absorbance evolution at 1eV

Figure 4: a) Bleaching of the WO_{3-x}/Ta_2O_5 composite film versus time in dark and b) corresponding absorbance evolution at 1eV

Figure 13: Absorbance variation at 1 eV after several hours without irradiation, study completed on 3 different cycles.

For the 3 first cycles, the absorbance at 1 eV (1200 nm) was recorded during the 12 hours following the colouring saturation under irradiation only. The cycling study demonstrates

that the shapes of the bleaching curves of the first, the second, as well as the third cycle are all almost identical. These results tend to show the good performance, in terms of stability of the film under successive cycles (colouring under irradiation+ bleaching under dark).

Conclusions

Huge photochromic properties of WO_{3-x} films obtained by dip-coating from suspended non-stoichiometric tungsten oxide nanopowder synthesized by a polyol chemical route have been investigated. The kinetic of the photochromism was studied. Several phenomena are responsible for two distinct kinetics of photochromism, the photoreduction of W^{6+} ions at the particle surface leading to intervalence charge transfer and the diffusion of the W^{5+} species within the bulk of the particles. The deposition of a layer of tantalum oxide on the WO_{3-x} films is decreasing the photochromic effect. In this later case, the top layer is proposed to limit the holes recombination with air water molecules or the surface O^{2-} anions departure. Cycling effect has been also demonstrated. This study opens the door to possible applications of non-stoichiometric tungsten oxide as smart windows or in smart textiles, which could progressively coloured during the day due to day-light

irradiation and self-bleached during nights or during a certain rest period in our cupboards.

Conflicts of interest

There are no conflicts to declare.

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